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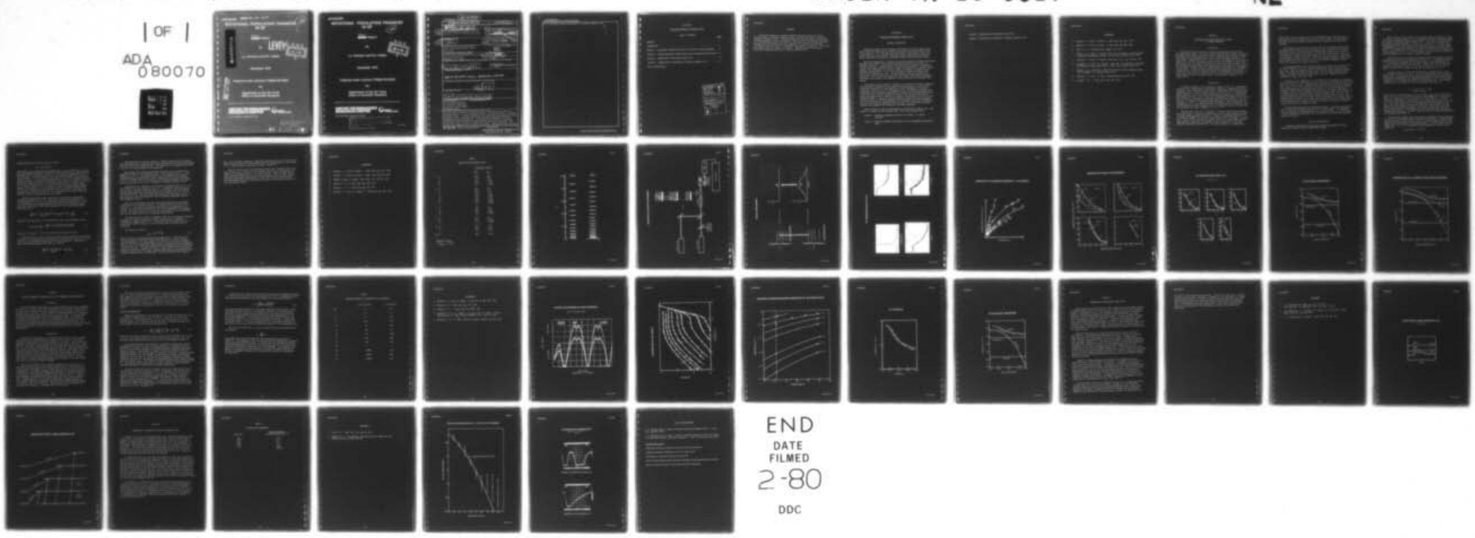

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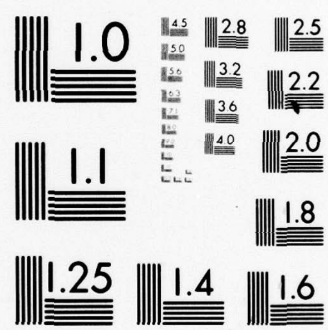

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ROTATIONAL POPULATION TRANSFER IN DF

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Final Report

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J.J. Hinchen and R.H. Hobbs

December 1979

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Prepared under Contract F49620-79C-0032

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[redacted] Report

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Collisional transfer of population between rotational levels of DF was measured using an i r double resonance method. The data were used to calculate rotational rates. Pressure broadening of DF absorption was determined for the fundamental lines P6 through P18. Total molecular collisional rates were obtained from the absorption data and compared with the total of individual collisional rates for velocity, vibrational and rotational relaxation. The results were compared with two kinetic rate models. Observation were also made

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Rotational Population Transfer in DF

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ABSTRACT

Collisional transfer of population between rotational levels of DF was measured using an IR double resonance method. The data were used to calculate rotational relaxation rates. Pressure broadening of DF absorption was determined for the fundamental lines P6 through P18. Total molecular collisional rates were obtained from the absorption data and compared with the total of individual collisional rates for velocity, vibrational and rotational relaxation. The results were compared with two kinetic rate models. Observations were also made of rotational lasing and vibration to rotation transfer in DF.

Rotational Population Transfer in DF

GENERAL INTRODUCTION

Chemical reactions between hydrogen and fluorine are used to pump excited states for HF/DF lasers and are capable of populating high vibrational levels in the range of v = 3-7 and high rotational levels. Populations in high rotational levels may relax towards a Boltzmann distribution through collisional energy transfer or by lasing on transitions between rotational energy levels.

Rates for deactivation of excited HF have been measured at United Technologies Research Center (UTRC) under a program sponsored by the Air Force Office of Scientific Research. In particular, rates have been determined for population transfer from upper vibrational states, among rotational levels, between velocity classes, from vibrational to rotational modes and transfer by lasing between rotational levels (Refs. 1 & 2). The techniques of laser fluorescence and double laser resonance are used. Several computer modeling programs use the data (Refs. 3-9) to calculate single line laser power, pulse laser time-energy-wavelength relationships, hole burning in power extraction and radiation linewidths.

The infrared double resonance technique for following rotational populations use absorption of radiation from a pulsed laser operating on a single v(1-0) vibrational transition to pump population in an HF gas sample to a specific rotational J level in the v = 1 vibrational level. Collisional processes then redistribute this population among other rotational and other vibrational levels. A CW probe laser is used to monitor the rate of loss of population from the pumped rotational level or the rate of arrival of population in one of the other rotational levels. Pressure broadened linewidths, which have been determined for HF by absorption of laser radiation, are a measure of the total collisional rate and can be used in comparison with the sum of the individual collisional transfer rates measured by fluorescence and double resonance.

Here we report on similar measurements to obtain kinetic data for DF. This report is divided into four sections which cover the following topics:

Section 1 Rotational Relaxation Studies of DF Using I. R. Double Resonance

Section 2 Pressure Broadened Linewidths for the DF Fundamental Absorption Band

Section 3 Observation of Rotational Lasing in DF

Section 4 Observation of Vibration to Rotation Transfer in DF

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SECTION 1

ROTATIONAL RELAXATION STUDIES OF DF USING I. R. DOUBLE RESONANCE

Introduction

Collisional transfer rates for rotational population were previously determined for HF (Ref. 1) by using a double laser resonance method. Population was pumped into an empty rotational level by radiation from a pulsed HF laser and arrival of this population into higher levels was monitored with a cw HF laser probe. Rotational levels J2, J3, J4 and J5 were pumped and levels probed ranged from J3 to J8. Rotational lasing from the level pumped to lower levels was observed and its effect on collisional transfer rates was evaluated (Ref. 2). The collisional transfer rates were satisfactorily described by a one parameter kinetic model. In this section we report parallel measurements for population transfer in DF. Since the rotational energy level spacings in DF are much closer than those in HF, as shown in Fig. 1-1, other molecular characteristics being almost identical, one would expect that rotational relaxation to be faster for DF.

Experimental

A schematic diagram of the experiment is shown in Fig. 1-2. Monochromatic radiation from a pulsed laser operating on a single P_{1-0} transition is used to illuminate a cell containing DF gas at 22°C. Absorption of the radiation pumps population from $\nu = 0$ into a single rotational level J of $\nu = 1$. Single wavelength radiation from a cw DF laser, which passes colinearly with the pulsed beam through the cell, is used to probe the absorption in various rotation levels and thus follows the change in population with time after the pulse. This is manifest as a change in transmitted laser intensity I. The DF population that is pumped to $\nu = 1$, J is redistributed by rotational relaxation processes. The vibration-rotation energy diagram in Fig. 1-2 illustrates various probing beam transitions for the case of pumping J = 3 of ($\nu = 1$).

The pump laser (Ref. 3) is a multipin, transverse flow, pulsed discharge type that utilizes a stream of premixed SF_6, D_2, and He and is grating tunable to produce single wavelength radiation. Single P_{1-0} wavelength pulses of 0.1 μsec duration (FWHM) at 12 pps each contain about 0.05 mJ of energy. The probe laser, which has been described in detail, (Ref. 4) is a small mixing device that radiates a single P_{2-1} wavelength cw beam containing 0.1-0.2 W with amplitude instability less than 3%. This laser operates on a single axial

cavity mode and can be tuned over the 350 MHz Doppler gain profile by use of a piezoelectric crystal mounted mirror in the optical cavity. The linewidth of the laser output is 10-30 MHz as measured with a scanning Fabry-Perot interferometer.

The tunability of the probe laser is a critical requirement because both the pulsed laser radiation used for pumping and the cw laser used for probing have narrow lines. Thus only molecules from a small section of the velocity distribution are pumped and in order to interact with this velocity class, the cw laser must be tuned to the same frequency as the pulsed output. This effect of the pumping is shown in Fig. 1-3. That the strongest absorption signals were obtained when the probe laser was tuned to line center is evidence that the pulse laser operates at or near line center.

The DF gas absorption cell was made from a Kel-F tube 40 cm in length with an internal diameter of 12 mm. Sapphire windows were held on each end with Kel-F wax. Kel-F was chosen because it was found in laser-fluorescence experiments to be immune to chemical attack by HF. The two laser beams were made colinear and passed through the long axis of the cell. Diameters of both pulsed and cw beams were about 3 mm.

Variations in the intensity of the cw laser due to absorption are monitored with an AuGe detector (77^oK) having a sensitive area 5 mm in diameter which intercepted the entire cw beam. Placed between the absorption cell and the detector were: first, a short cell containing high pressure ($\sim$ 1 atm) DF gas to diminish P_{1-0} pulsed radiation by absorption and second, a 1/4 meter spectrometer to eliminate residual pulsed radiation and pass the P_{2-1} cw beam. The detector has a response time of 2-3 nsec; signals from this detector were fed into an oscilloscope amplifier (Tetronix 7A15A) having a response time of 5 nsec. The overall system rise time of less than 10 nsec is a factor of 10 shorter than the shortest measured signal time. Data were recorded as pictures of scope traces for individual pulses. Repetitive traces for pulses at constant DF pressure varied less than 5% from pulse to pulse.

The gas handling system was also made from Kel-F. Pressures were measured with a capacitance manometer calibrated with a McLeod gauge. The procedure used for purifying DF (Ozark-Mahoning Co.) is given in Ref. 5. The HF content in the DF samples was determined to be less than 3% by absorption measurements using a cw HF laser.

Results and Discussion

Intensity measurements of probe laser radiation were made to follow population changes in various experimental regimes.

Typical data are shown in Fig. 1-4 for several values of pressure. These traces are of temporal changes in the transmitted intensity of probe radiation as a result of relaxation after pumping level J. The probe laser monitors the population difference between $\nu = 2$ and $\nu = 1$. Since the $\nu = 2$ level of DF is unpopulated during the rotational equilibration time, the observed changes in absorption are a direct reflection of changes in population in the probed level. It is evident from the traces of Fig. 1-4 for the case of pumping with J2 and probing at J10 of $\nu = 1$ with DF pressure varied from 0.07 to 0.33 torr, that the transfer time is longer at lower DF pressures.

Values for the rate of population transfer between rotational levels were obtained from traces such as those shown in Figs. 1-4. An exponential growth of the absorption was assumed and the time constant τ was obtained at the $(1 - 1/e)$ point of maximum signal decrease. Similar data were recorded for transfer in DF from J2 to J4, 6, 8, 10; from J3 to J5, 6, 7, 8, 9, 10, 11; from J4 to J5, 6, 8, 10; from J5 to J8, 10; and from J6 to J7, 8, 9.

The data on Fig. 1-5 show that the increase of transfer rates is not quite linear with pressure. Also, the data at low pressure do not extrapolate through zero. At high pressure the shortened absorption time constants are significantly influenced by the pumping pulse duration. At very low pressure, diffusion out of the probe beam adds to the absorption decay. The measured transfer time τ is related to a corrected transfer time τ_{corr} by

$$\frac{1}{\tau} = \frac{1}{\tau_{corr} + \tau_{pulse}} + \frac{D}{P},$$

where D is the diffusion rate out of the cw beam, τ_{pulse} is the pulse decay time, and $1/\tau_{corr}$ is the transfer rate for a zero width pulse. The value of $1/P\tau_{corr}$ is then taken to be a constant for a given data set. The best fits of this expression to the data for $1/\tau$ versus pressure are shown in Fig. 1-5. This figure shows some of the experimental data for pumping J3 that were used in the analysis; actual data points are represented by the small numbers which code the level probed. The constant values used for D and τ_{pulse} were determined by multiparameter fits of the data sets yielding D = 5790 torr/sec and τ_{pulse} = 65 nsec. These are near the values used previously for fitting HF data (Ref. 1).

The corrected transfer times are measured at population values relative to the value in the probed level at rotational equilibrium. A simple approximation for deriving rate constants from τ_{corr} can be obtained from the rate equation for the population of the probed level j. At short times, only the pumped level i of $\nu = 1$ is populated and the population of level j can be written as

$$n_j = n_o \pi_j \, (1 - e^{-t/\tau_{ij}});$$

substituting this in the rate equation we find

$$k_{ij} = \bar{n}_j \, (1/P\tau_{ij}),$$

where $(1/P\tau_{ij})$ is the rate from the pumped level i to the probed level j, n_o is the initial pumped population corrected for pulse duration, $\bar{n}_j$ is the normalized Boltzmann factor for the state j,and k_{ij} is the simplest approximation to the rate constants. Corrected values for $1/\tau$ were used to obtain k_{ij} and these are listed in Table I. A more accurate determination of the rate constants from the measured transfer rates could be obtained by the solution of a number of simultaneous linear equations; however, this would require data for transfer times to the lower J levels (J = 0, 1,2) which were not measured because rotational lasing to lower levels of DF was observed. Rather, a phenomenological model for the rate constants was developed and fitted to the data. This model then provides rate constants not only for the experimentally accessible levels but provides a means of extrapolation to other levels.

A general equation was first developed to describe the experimentally determined transfer rates for HF. The physical concept employed was that an excited molecule in v = 1, J_1 collided with a ground state molecule in v = 0, J_o and both molecules changed rotational states with the nonresonant energy going into translation. With that assumption the rate equations governing the process were:

$$\frac{d}{dt} n_j^{v=1} = \sum_{i \neq j,k,l} \left(n_k^{v=0} n_i^{v=1} K_{ijkl} - n_k^{v=0} n_j^{v=1} K_{jikl} \right) \qquad (1)$$

where n_j^v is the population in the vibrational state v and rotational level j,

$$K_{ijkl} = K_o \bar{n}_j \bar{n}_l e^{-\left|\left(E_j^{v=1} - E_i^{v=1}\right) + \left(E_l^{v=0} - E_k^{v=0}\right)\right|/kT} \qquad (2)$$

where K_o is a constant. $\bar{n}_j$ is the normalized Boltzmann population.

This definition of vc_{ijkl} satisfies detailed balance explicitly and assumes the rate to be proportional to the exponential of the energy defect in the collision (i.e. to the energy transferred to or from translation). Summing Eq. 1 over the unobserved ground state levels one obtains

$$\frac{d}{dt} n_j^{v=1} = P \sum_{i \neq j} \left(n_i^{v=1} K_{ij} - n_j^{v=1} K_{ji} \right). \qquad (3)$$

Using this model of the rate constant a computer simulation of the experiment was carried out, including terms in the rate equation to describe the pumping pulse and the velocity redistribution. The population of rotational levels from $J = 0$ to $J = 15$ were included in the simulation.

Experimental rate constants previously determined for HF transfer from pumped J to probed J' are presented in Fig. 1-6 for pumping J=2, 3, 4, 5, and probing up to J' = 8. The lines marked H-H in the figure are the computer simulation results using equation 2 and a single value for the rate constant K_o of $2.0 \times 10^{-8} sec^{-1} torr^{-1}$. The model is in reasonable agreement with experimental results and can be used to extrapolate to higher rotational levels.

Experimental rate constants for DF obtained by pumping levels J3, 4, 5, 6, 7, and probing to J11 are presented in Fig. 1-7. To simulate these results the value of K_o in equation 2 was corrected for the difference in dipole moments and molecular velocities between HF and DF; this results in $K_o = 1.6 \times 10^{-8}$ $sec^{-1} torr^{-1}$ for DF. With this single modification the lines (H-H) in Fig. 1-7 were obtained; these calculations are also in reasonable agreement with the DF experimental results.

The rate of population loss from a particular pumped level (rotational relaxation) can be calculated from Eq. 2 by summing the rates from J to all values of J'. These are the rotational relaxation rates designated by H-H in Figs. 1-8 and 1-9 for DF and HF, and are in fair agreement with linewidth values. The solid portion of the lines are calculations for the experimental data and the dashed portions are extrapolated calculations.

The kinetic model of Polanyi and Woodall (Ref. 6) for rotational relaxation is based on a complete transfer of energy to translation as a molecule collisionally changes levels by ΔJ. This model was first proposed for the deactivation of HF by argon but it has also been used to describe self deactivation.

The rate K_{ij} is given by

$$K_{ij} = Ae^{-B\,\Delta E/RT} \qquad (4)$$

where A and B are constants and ΔE is the energy for ΔJ. This form of the rate K_{ij} applies for positive ΔE while detailed balance is used to supply K_{ij} for negative ΔE. By substituting Eq. 4 into Eq. 3 rates for HF transfer from J to J' were calculated and these results are shown as the line designated by P-W in Fig. 1-6. This model seems to fit the experimental data for HF about as well as our model. However, in order to obtain a good fit to DF data new values for A and B had to be used; a simple correction for dipole and molecular velocity differences was not sufficient. With this change the P-W lines in

Fig. 1-7 for DF were calculated. Rotational relaxation rates for DF and HF were also calculated using the Polanyi-Woodall model by summing from J to all values of J'. These results are also shown in Figs. 1-8 and 1-9.

Both our theory and the Polanyi-Woodall theory give reasonable fits to the data in Figs. 1-1, 1-2 and 1-5, 1-6, although the basic rate constant for P-W needed to be changed in order to fit both HF and DF. These two theories give vastly different predictions for rotational relaxation rates at high J levels. Additional experimental measurements at these high J levels should provide differentiations between the calculations and may give information needed for a more comprehensive theory.

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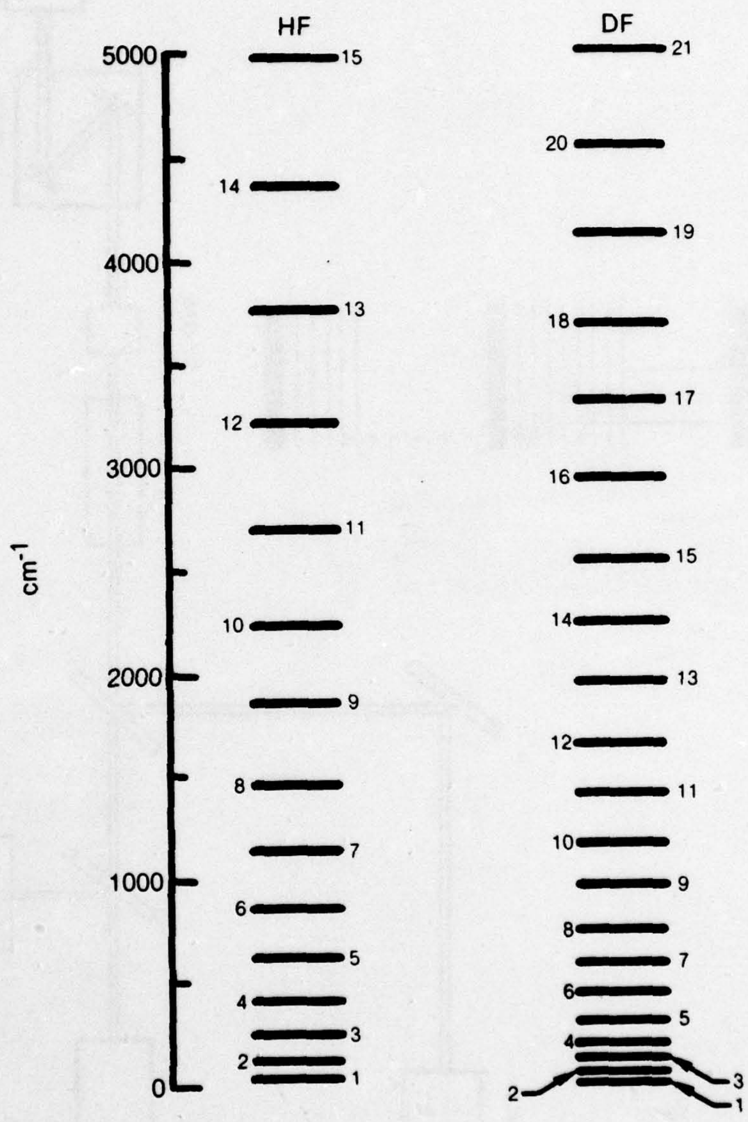
TABLE I

TRANSFER RATE CONSTANTS FOR DF

	($\times 10^6$ sec^{-1} torr^{-1})	
	$1/P\tau$	K_{ij}
2 → 3	157.6	30.3
4	73.0	11.8
6	27.9	2.06
8	16.0	0.321
10	10.7	0.0341
3 → 4	176.1	28.6
5	74.2	8.7
6	41.8	3.08
7	25.3	1.03
8	15.2	0.305
9	13.9	0.122
10	12.6	0.0430
11	10.4	0.0124
4 → 5	73.3	8.6
6	34.3	2.53
8	21.5	0.431
10	14.5	0.0495
5 → 6	177.4	13.1
8	36.7	0.736
10	14.1	0.0481
6 → 7	83.5	3.41
8	52.5	1.05
9	35.7	0.313
8 → 9	86.9	0.761

Assume D = 5790.5
τ_{pulse} = 65 ns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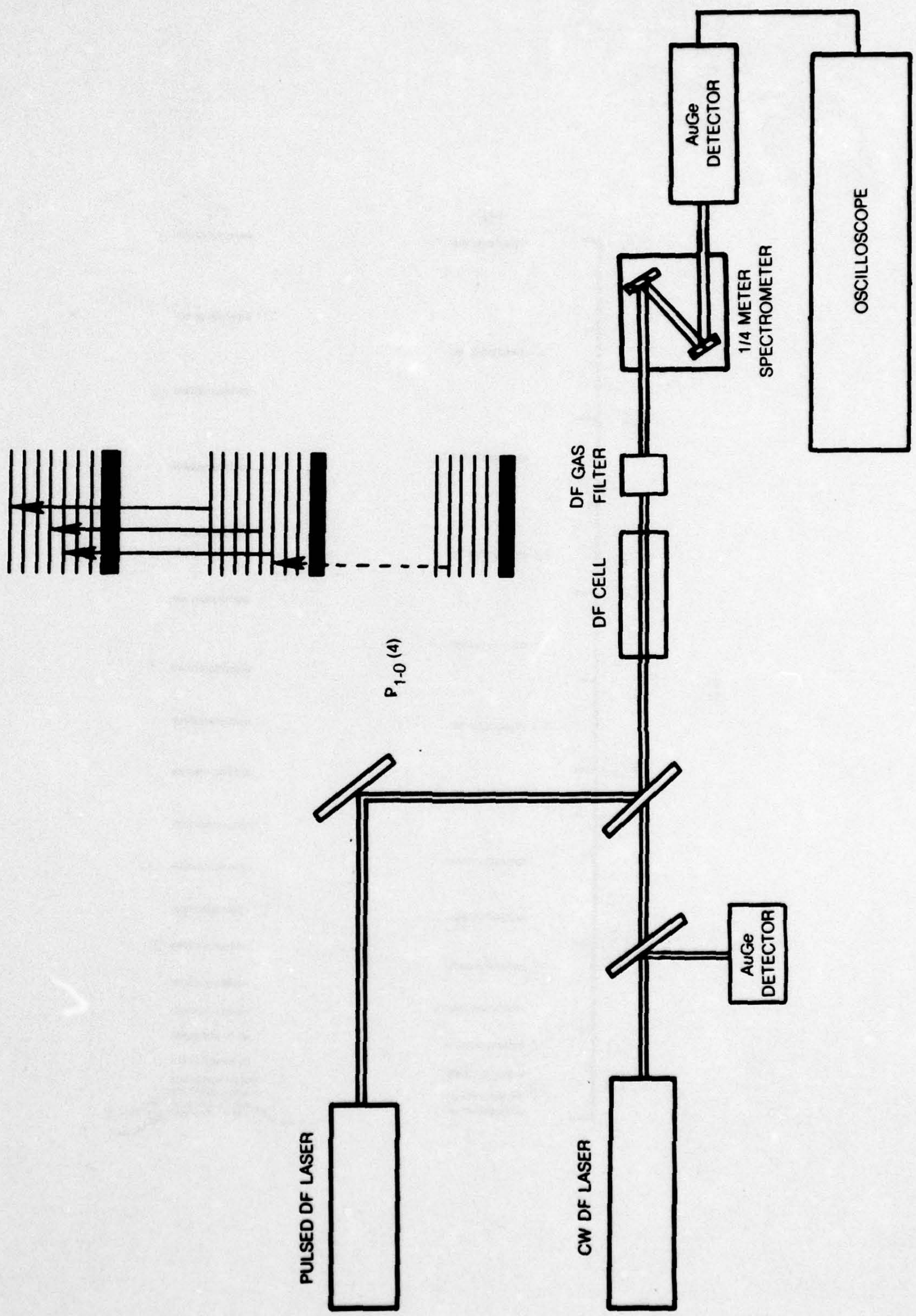
ROTATIONAL RELAXATION EXPERIMENT



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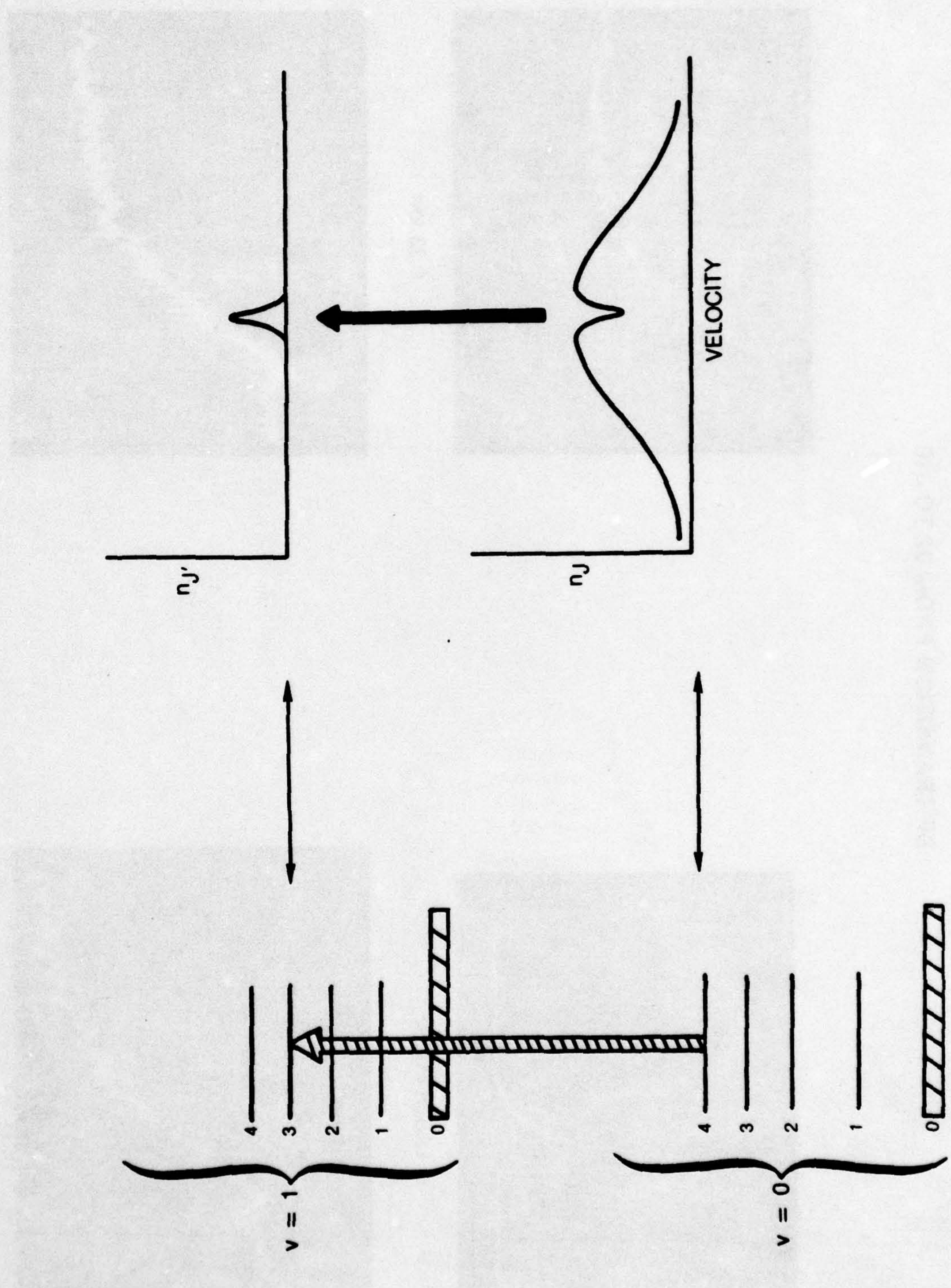
PULSE LASER PUMPING



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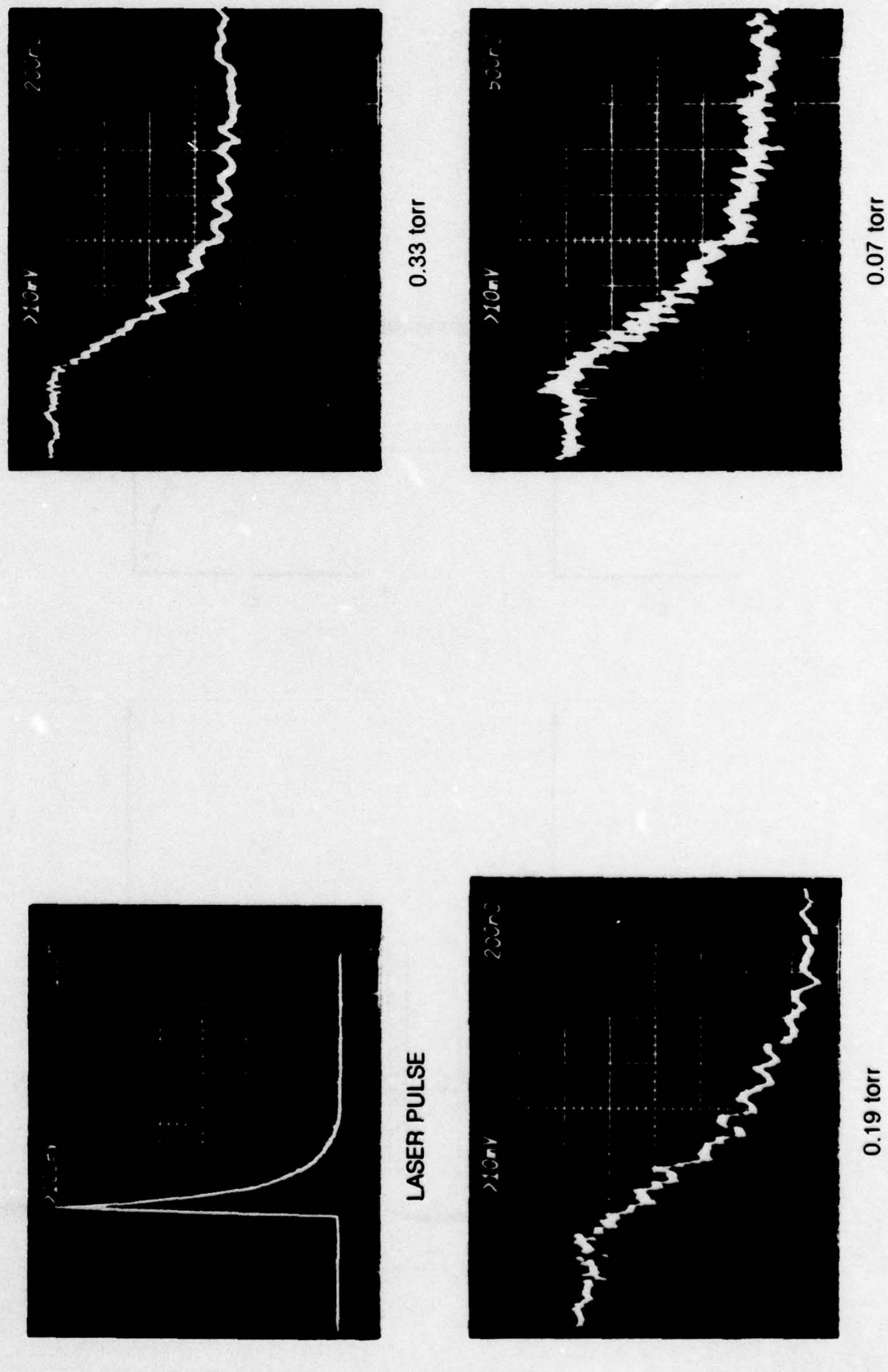
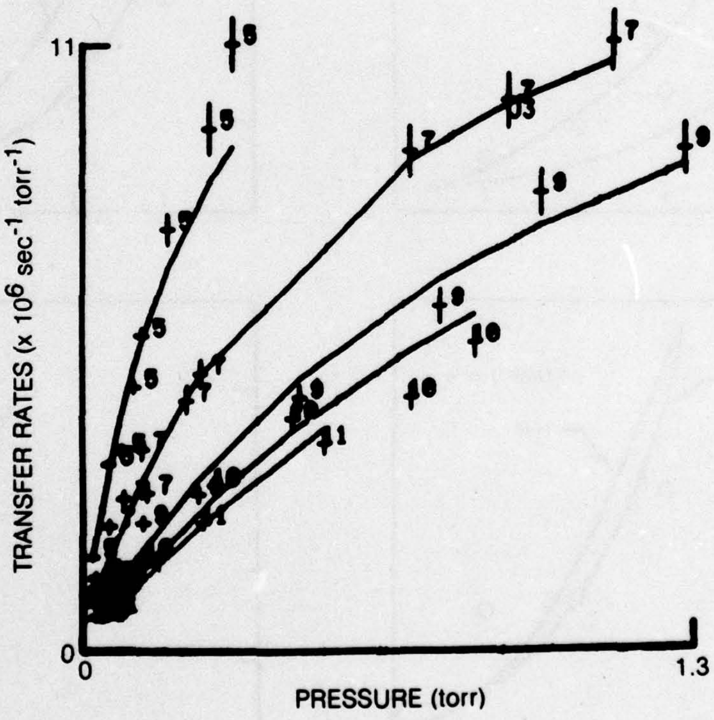
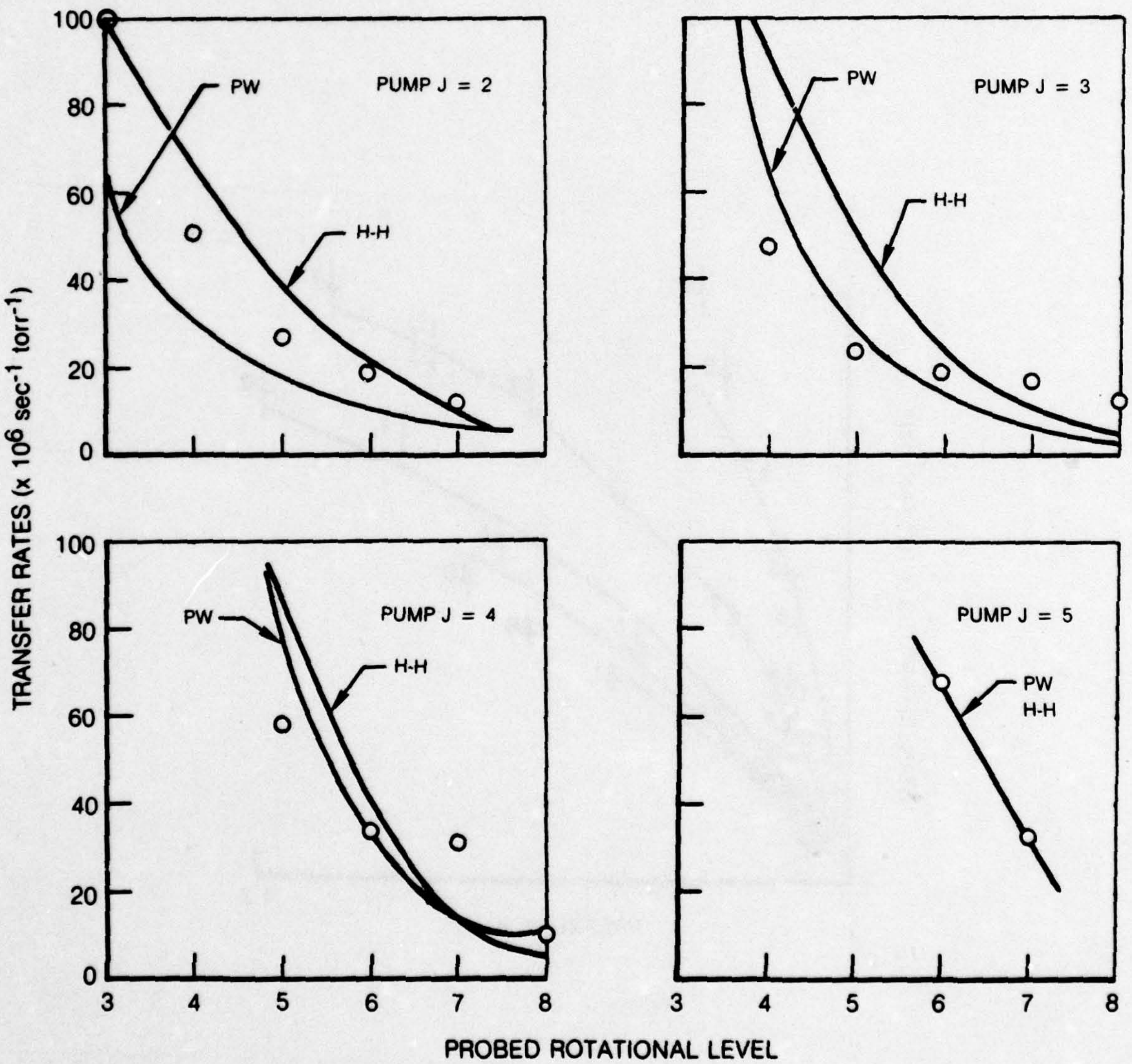


COMPUTER FIT OF PRESSURE DEPENDENCE — DF TRANSFER

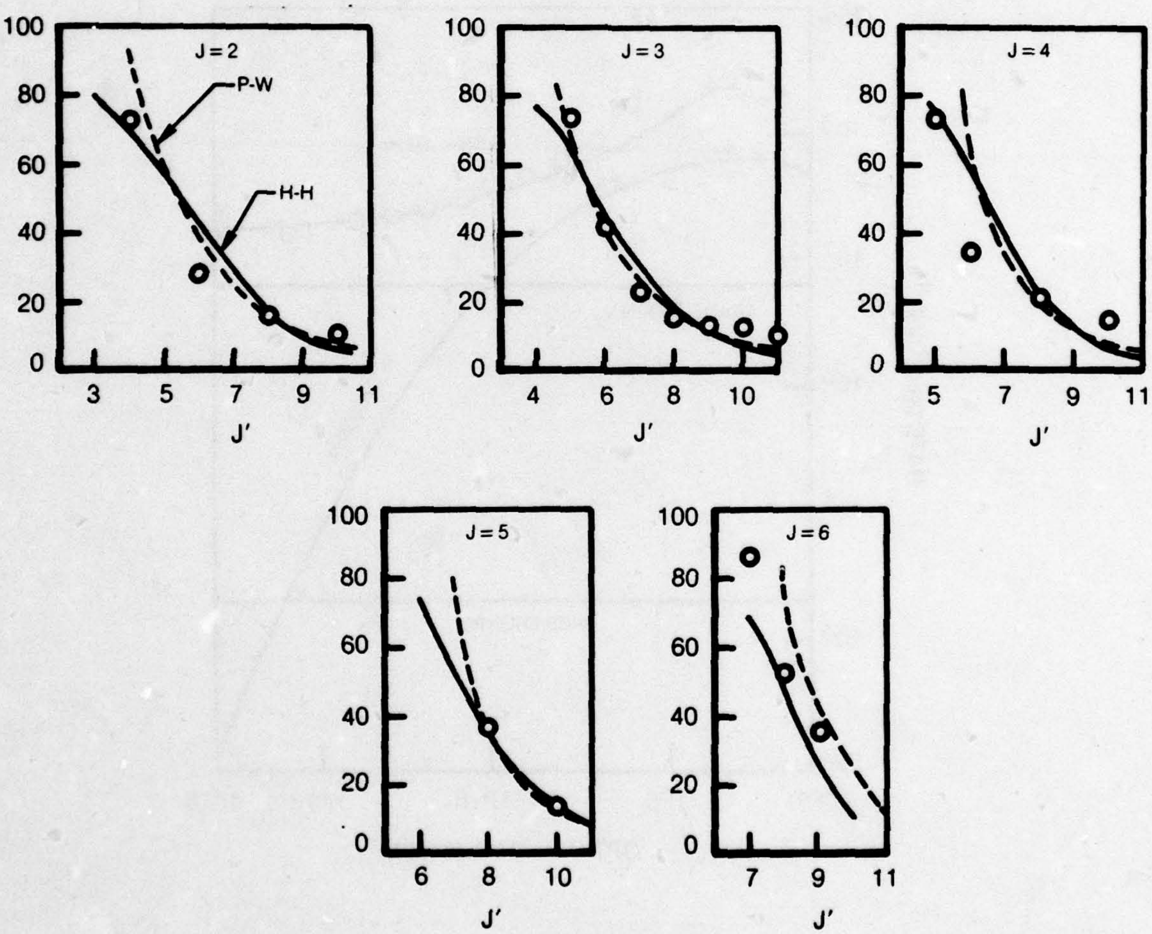


COMPARISON OF MODEL AND EXPERIMENT

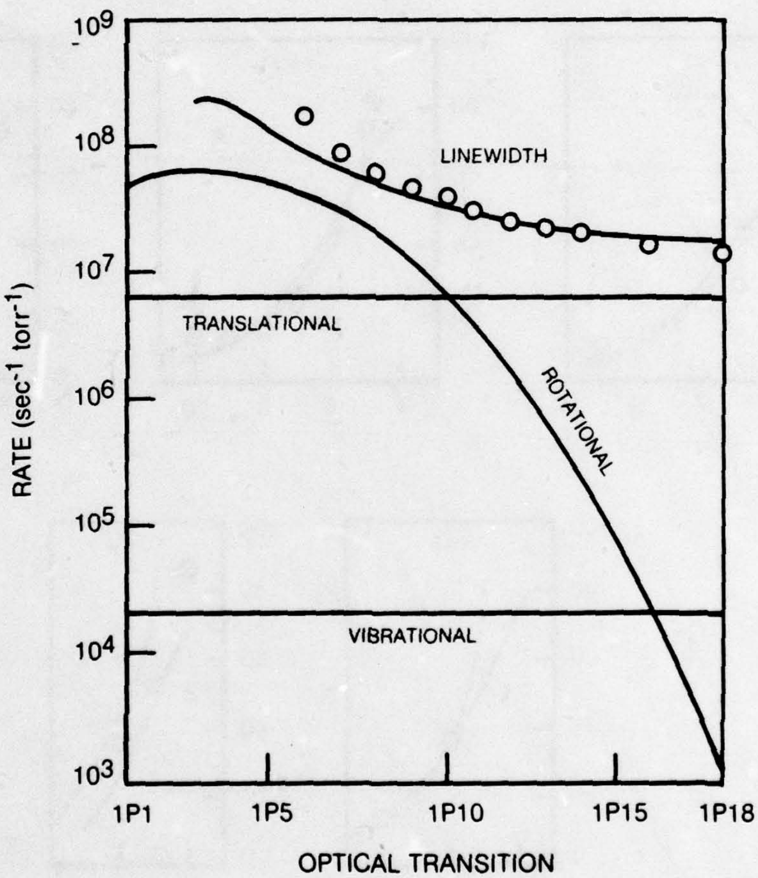


DF TRANSFER RATES FROM J TO J′

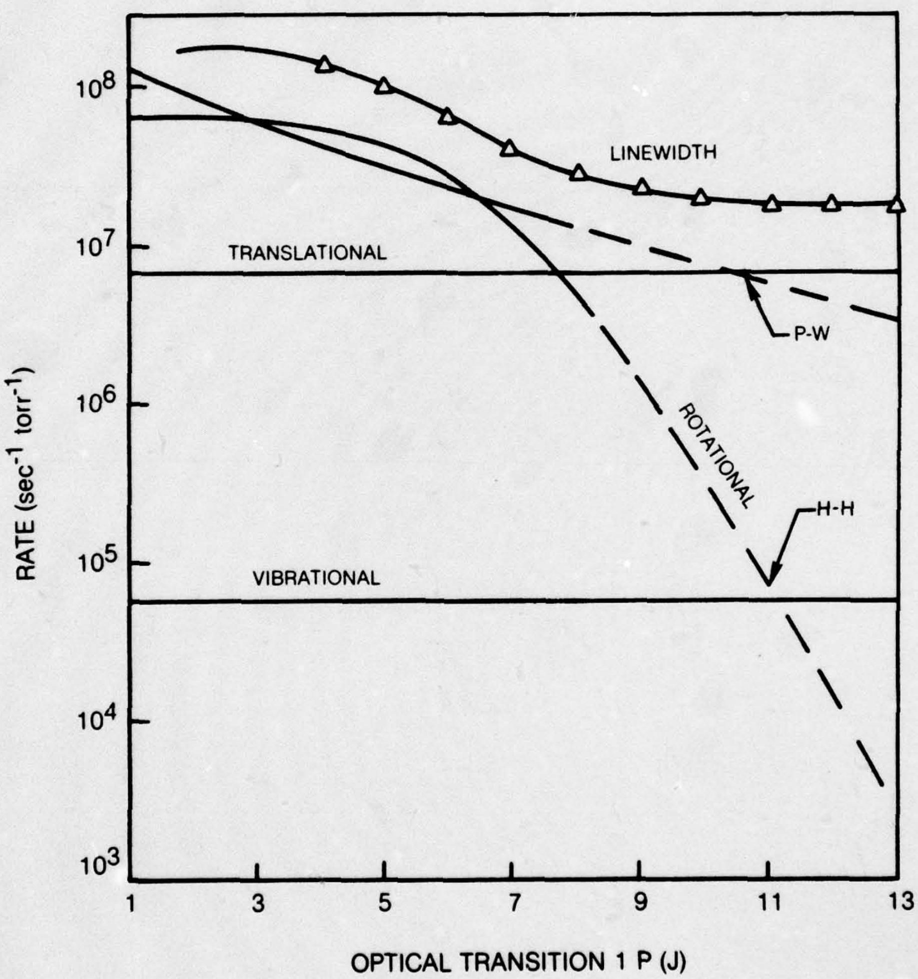
(10^6 sec^{-1} torr^{-1})



DF COLLISIONAL FREQUENCIES



CONTRIBUTIONS TO HF LINEWIDTH FROM VARIOUS PROCESSES



SECTION 2

PRESSURE BROADENED LINEWIDTHS FOR THE DF FUNDAMENTAL ABSORPTION BAND

Introduction

Collision broadened linewidths are a useful measure of the total collisional processes in a gas and can be used in comparison with individual rates measured by other means. Data for HF and DF linewidths are of particular interest for chemical laser technology. We have recently reported measurements of broadening parameters for HF gas using a narrow line cw HF laser (Ref. 1). Bonczyk (Ref. 2) has made similar measurements for DF fundamental band over the range of transitions P5 through P10. There is considerable interest in data for high DF lines for both the laser needs and as a source of collisonal rates. In this section we describe results from laser measurements over the range P6 through P18 and a comparison of the derived collisional rates with data from other measurements.

Experimental

Absorption was determined by directing radiation from a cw laser through an absorption cell and measuring the changes in the intensity of the laser beam with an InSb detector as DF gas was added to the cell. The incident beam intensity was monitored by splitting off part of the incident beam to a second detector. The laser, a small mixing type producing single line cw radiation of 0.1 - 0.2 watts, has been described previously (Ref. 3). The laser cavity optics consisted of a grating for line selection and a concave copper mirror (0.6 M radius) mounted on a piezoelectric crystal for cavity tuning. Radiation was extracted from the cavity by specular reflection from the grating. A 1/2 meter Jarrell Ash Spectrometer was used to identify laser lines. The laser oscillated on a single longitudinal mode with a linewidth of less than 10 MHz and could be tuned over a range of 350 MHz.

A series of absorption cells varying in length from 0.22 cm to 65 cm were made from Kel-F tubing with sapphire windows held in a compression seal. For the weakest absorption, two 65 cm cells were used in series in a folded configuration. For higher temperature measurements, the cells were heated in a tubular oven that varied in temperature less than 1 C (at 100 C) along its 90 cm length. The gas handling system was also made from Kel-F. A capacitance manometer calibrated with a McLeod gauge was used to measure gas pressure. DF (Matheson Co.) was purified by distillation between vessels at 77K and 190K, followed by absorption and desorption from NaF and then pumping at 77K before each use to remove H_2. The HF content in the DF samples was less than 3% as measured by absorption with a cw HF laser.

Data were recorded by displaying detector signals for the incident intensity, I_o, and the transmitted intensity I on a dual beam oscilloscope and photographing the traces as the laser was swept over the power-frequency curve. Line center was easily identified by a Lamb dip which is clearly visible in the sample trace shown in Fig. 2-1. Because the traces were taken simultaneously, fluctuations in laser intensity did not affect the ratio I/I_o used to calculate the absorption coefficient α from $I/I_o = e^{-\alpha L}$ where L is the cell length.

Results and Discussion

Absorption measurements in DF were made for the lines P6 through P14 at 23C over pressure ranging from 0.1 torr to 750 torr. The data for line center absorption, α_o, are presented in Fig. 2-2 as a plot of α_o versus P. In the Doppler region, α_o is a constant and the data are in excellent agreement with the straight lines that are drawn using values from

$$\alpha_o = - \frac{C^2 A}{8\pi \nu_o{}^2} \left(\frac{MC^2}{2\pi kT}\right)^{1/2} \left(N_u - \frac{g_u}{g_\ell} N_\ell\right) \qquad (1)$$

where A is the Einstein coefficient whose values are from Meredith (Ref. 4) and ν_o is the line center frequency, M is the molecular mass, N_u and N_ℓ are upper and lower level populations and g_u and g_ℓ are the level generacy factors.

At increased pressure the absorption is dominated by degeneracy pressure broadening and the data in Fig. 2-2 become asympotic to constant value of α_o. With further increase in pressure, HF polymer formation contributes additional absorption which is more evident for higher lines where absorption from the monomer is weaker. The data for higher P lines were corrected to obtain pressure broadened absorption for the monomer by subtracting the polymer contribution. Absorption for the lines P12, P13 and P14 are completely dominated by polymer absorption above 200 torr and exhibit increasing absorption with pressure independent of absorption line. This behavior is nearly identical with observations for HF. High pressure absorption data for P12 were corrected to obtain pressure broadened absorption by subtracting the polymer contribution.

For lines higher than P12 this procedure could not be used because of the preponderence of polymer absorption at 23 C. Measurements were made at 100 C for P13 through P18 and extrapolated to 25 C by accounting for the effect of temperature change on the absorption coefficient due to change in molecular density, velocity and rotational population distribution. These factors give a functional dependence of $T^{-1}e^{-E/RT}$. The collisonal cross section was assumed to be temperature independent. This function was found to fit HF data up to 100 C in Ref. 1 and shows a good fit through data for DF at P12 over the range of 23 C to 100 C in Figure 2-3.

Linewidths were calculated from values for the pressure broadened absorption α_o (cm^{-1}) at the line center for the lines P6-P18 at 23 C. By assuming a Lorenz line shape which relates the line width (HwHh) and line center absorption:

$$\Delta\nu = \frac{760A}{\alpha_o \; 8\pi^2 CE^2} \left(\frac{2J-1}{2J+1}\right) N_J \tag{2}$$

where the negligible population in the upper level has been neglected. Values from Meredith were used for A, the Einstein coefficient, and E, the energy separation for the transitions; the population in the lower rotational level N_J for the transitions was calculated from the Boltzman distribution at the appropriate temperature. The resulting linewidths are listed in Table I and are plotted in Fig. 2-4 for the P branch lines P6 through P18. Calculations by Meredith (Refs. 4, 5) using the Anderson theory of linewidths provides the solid line in Fig. 2 which is an excellent description of the experimental data.

The total collision rate, ν, can be obtained from the line width from the relationship

$$\nu = \frac{2\pi C}{760} \Delta\nu$$

Collisional rates for DF obtained from the absorption data are shown in Figure 2-5. For comparison, rates are also plotted for vibrational, rotational and translational relaxation rates. The latter two were obtained from double resonance measurements as described in the previous section. The sum of these three rates are within a factor of two of the linewidth. This deviation can partially be explained by uncertainties in velocity relaxation rates and by absence of exchange collisions in the rotational rates which are included in the linewidths.

TABLE I

PRESSURE BROADENED DF ABSORPTION AND LINEWIDTHS

	α (cm^{-1}) (23°C)	$\Delta\nu$ ($cm^{-1}atm^{-1}$)
1P6	6.2	.44
7	4.2	.37
8	3.1	.258
9	1.84	.201
10	.87	.165
11	.39	.131
12	.147	.106
13	.051	.096
14	.015	.085
15	--	--
16	.00085	.074
17	.00020	.062
18	.000035	.061

REFERENCES

1. Hinchen, J. J. and R. H. Hobbs: J. Opt. Soc. Am. 69, 1546, 1979.

2. Bonczyk, P. A.: Phys. Rev. A11, 1522, 1974.

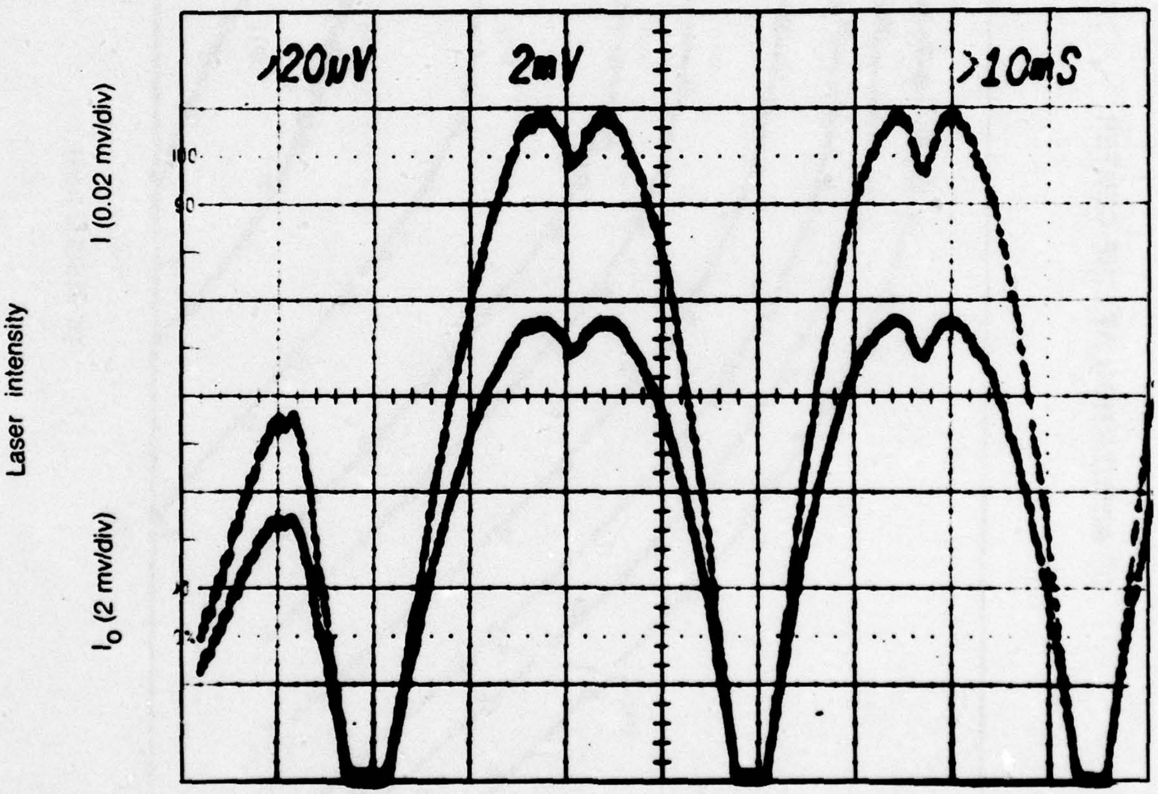
3. Hinchen, J. J.: J. Appl. Phys. 45, 1818, 1974.

4. Meredith, R. E., T. S. Chang, F. G. Smith, and D. R. Woods: Science Applications, Inc. Report SAi-73-004-AA(I), Vol. I and II, 1973.

5. Meredith, R. E.: J. Quant. Spectrosc. Radiat. Transfer 12, 485, 1972.

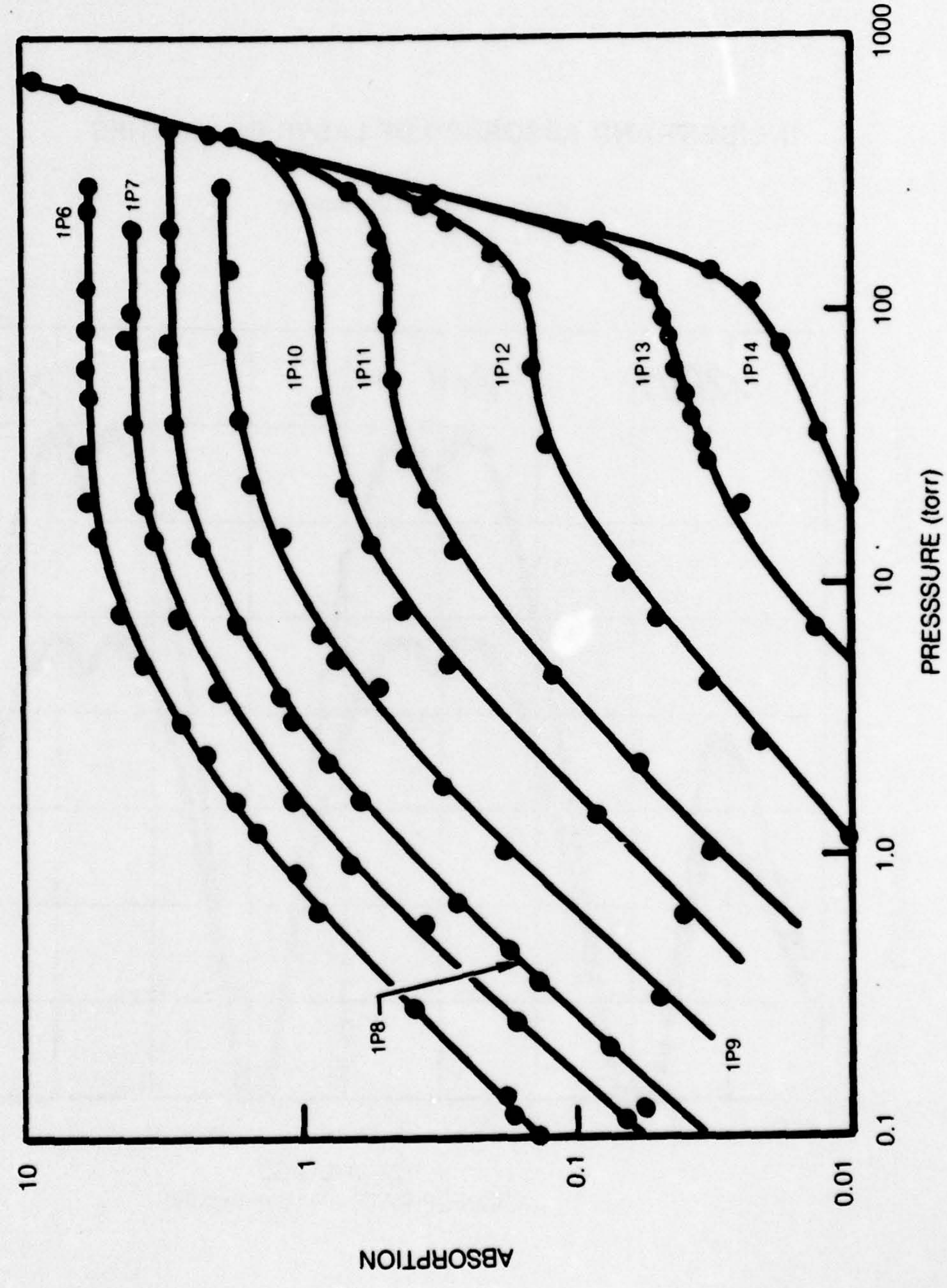
INCIDENT AND ABSORBED DF LASER INTENSITIES

LINE 1P12, DF PRESSURE 400 torr

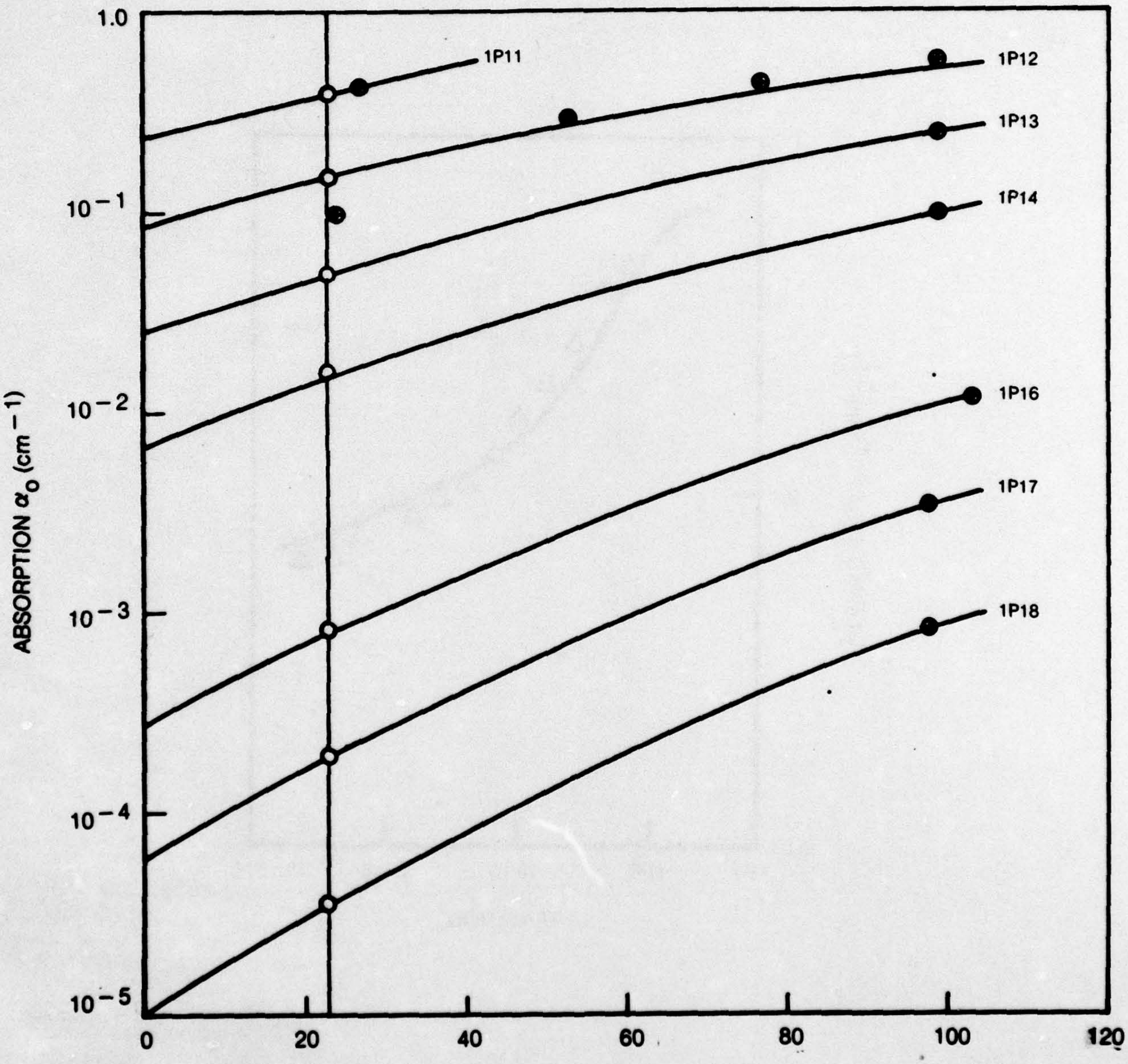


PZT VOLTAGE
(SWEEP RATE — 10 msec/div)

DF ABSORPTION AT LINE CENTER



VARIATION IN PRESSURE BROADENED ABSORPTION AT LINE CENTER FOR DF



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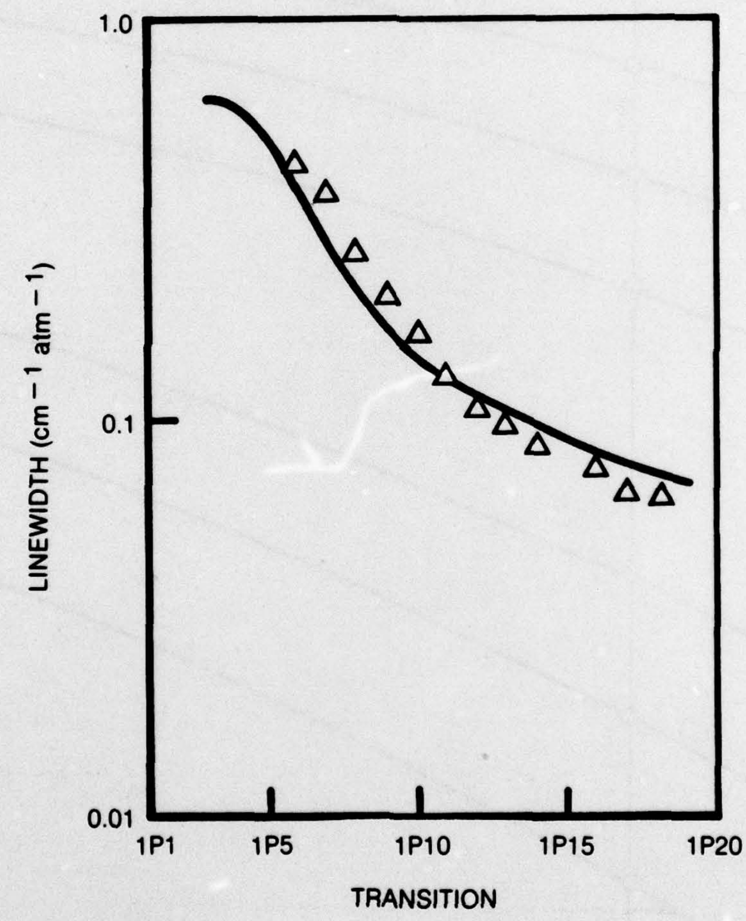
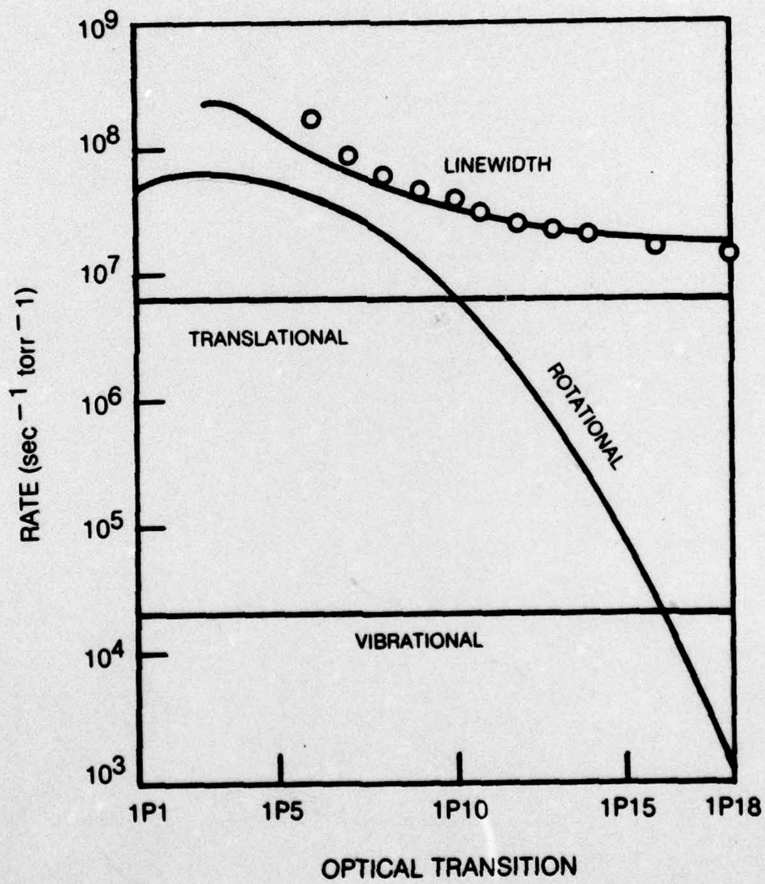
DF LINEWIDTHS



DF COLLISIONAL FREQUENCIES



SECTION 3

OBSERVATION OF ROTATIONAL LASING IN DF

Lasing between rotational levels in HF/DF chemical lasers has been reported by several authors (Ref. 1) and this may be a common feature of these high gain systems. Skribanowitz (Ref. 2) has described rotational lasing or superfluorescence in HF gas samples pumped by radiation from a pulsed HF laser under conditions used in collisional relaxation studies. We have previously reported (Ref. 3) population transfer in HF by both collisional and radiative processes in ir laser double resonance experiments. Lasing at long wavelengths was observed after pumping an HF gas sample with each of 1P3 through 1P8 transitions. No distinction was made between lasing, superfluorescence or superradiance in the experiments. The effect of "lasing" on population transfer was incorporated in a kinetic model.

Similar observations of "lasing" between rotational levels in DF are reported here. The experimental apparatus described in reference 3 was used which employed a Kel-F gas sample cell 40 cm in length. A pumping pulse from a DF laser was passed through the cell which was fitted with CaF_2 windows and contained a sample of DF. The excited DF "lased" on rotational transitions producing long wavelength radiation that was reflected by the CaF_2 windows and transmitted out of the cell through a polyethylene window which is not transparent to the short wavelength pumping pulse. A GeGa detector (4^oK) was used to observe the long wavelength "lasing" and individual lines were identified by use of a monochrometer (Perkin Elmer Model E1). With the particular grating available for use, the monochrometer passed only radiation wavelengths between 100 and 200 microns.

"Lasing" at long wavelengths was observed after pumping the DF gas sample with each of 1P4 through 1P7 transitions. Cascading from one level to lower levels was definitely seen. In Figure 3-1 an example of cascading is shown with traces from detecting a 1P5 pumping pulse and long wavelength pulses from J4→3 and J3→2 of v=1 at 118 microns and 158 microns. There is a definite delay between the start of the long wavelength pulses which is probably a reflection of the required time to build up population in J3 from the J4→3 radiative transfer of population. Cascading was not directly observed in the radiative transitions for HF but was evident in population transfer to lower levels ($\Delta J=-2$) as measured with a probe laser (Ref. 3).

The experiments with DF are summarized in Fig. 3-2. On pumping with 1P4, "lasing" from J3 to J2 (v=1) was recorded. Pumping J4 with a 1P5 pulse produced lasing on both J4→3 and the cascaded transition J3→2. When J5 was pumped by a 1P6 pulse, "lasing" from J5→4 at 95 microns was not observed because of the limitation of the monochrometer, however the transition J4→3

did "lase" at 118 microns and 158 microns. From this we infer that a "lasing" cascade J5→4→3 occurred. Similarly, on pumping J6 the observation of "lasing" at 118 microns on the J4→3 transition leads to the conclusion that there was "laser" cascading J6→5→4→3. The kinetic model simulation of the experiment (Ref. 3) had predicted cascaded lasing three or four levels below the pump level for both HF and DF. This experimental evidence now confirms that prediction.

REFERENCES

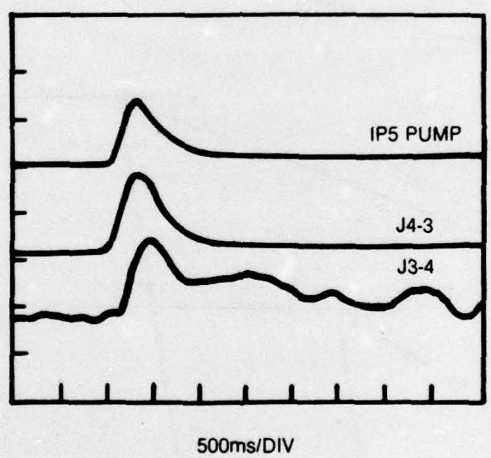
1. T. F. Deutsch; Appl. Phys. Lett. 11, 18, 1967.
   O.R. Wood and Y. T. Chang Appl. Phys. Lett. 20, 77, 1972.

2. N. Skribanowitz, I. P. Herman, R. M. Osgood, M. S. Feld and A. Javan; Appl. Phys. Lett. 20, 428, 1972.

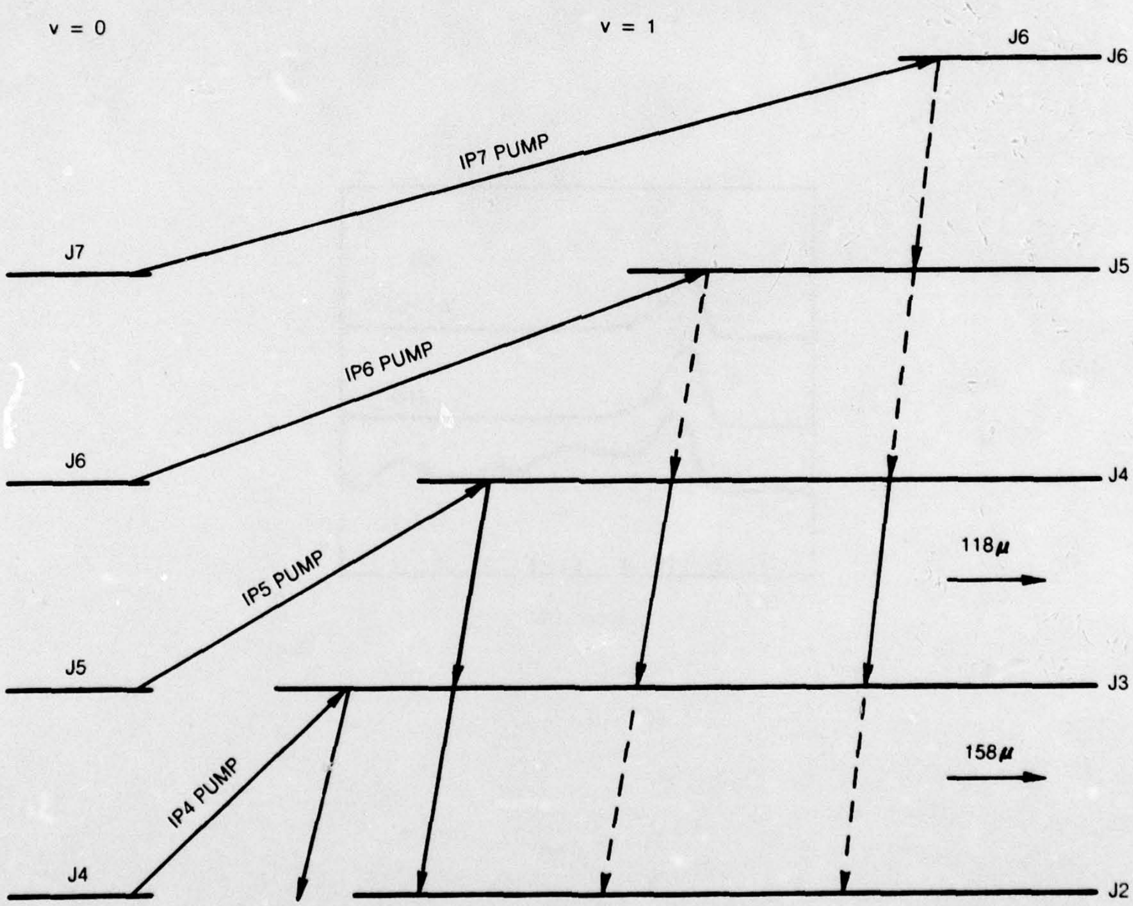
3. J. J. Hinchen and R. H. Hobbs; J. Appl. Phys. 50, 628, 1979.

DF ROTATIONAL LASING CASCADE J4-3, J3-2

DF = 0.005 torr



OBSERVED ROTATIONAL LASING TRANSITION IN DF



79–12–120–15

SECTION 4

OBSERVATION OF VIBRATION TO ROTATION TRANSFER IN DF

In order to account for the exceptionally fast vibrational relaxation rates of HF and DF, a mechanism was proposed by Shin (Ref. 1) and by Wilkins (Ref. 2) whereby a resonant transfer of population would occur from v to v-1 at high J rather than requiring all of the vibrational energy to go into translation. As an example, in HF vibrational relaxation would occur by a transfer from v=1 to v=0 at J14. There are other nonresonant mechanisms that may occur; an excited molecule in v=1, J3 may collide with a ground state molecule v=0, J3 and the colliders may share the energy leaving both molecules in v=0, J10. Other non-resonant energy sharing collisions are also possible.

A preliminary search has been made to determine the rotational distribution in v=0 of HF and DF by probing this manifold with the cw laser after pumping population into v=1 with pulsed laser radiation. Results are shown in Fig. 4-1 for HF after pumping with 1P4 and probing with the laser transitions 1P4 through 1P13. The solid line indicates the equilibrium Boltzmann distribution; an excess above the distribution which can be seen for the highest levels is direct evidence for vibration to rotation transfer at high J for at least some of the v=1 population. For DF an example is shown of intensity traces of the cw probe laser in Fig. 4-2. The top trace is the incident intensity as the laser is swept over the linewidth and the lower trace shows the intensity change at line center as population arrives in J11 of v=0 after pumping J3 of v=1.

The maximum in the intensity from such traces was measured probing the DF levels J10,11,12,13,14 of v=0. These data were used to calculate the amount of population flowing into each rotation level as an excess over the Boltzmann distribution. Results from measurements at three pressures, 0.09, 0.12 and 0.27 torr are averaged in Table I. These data show that for DF the percent excess is the same for all levels and indicate that the population in v=1 transfers to v=0 essentially in a Boltzmann distribution without preferential transfer to particular rotation levels.

TABLE I

V-R POPULATION TRANSFER DF

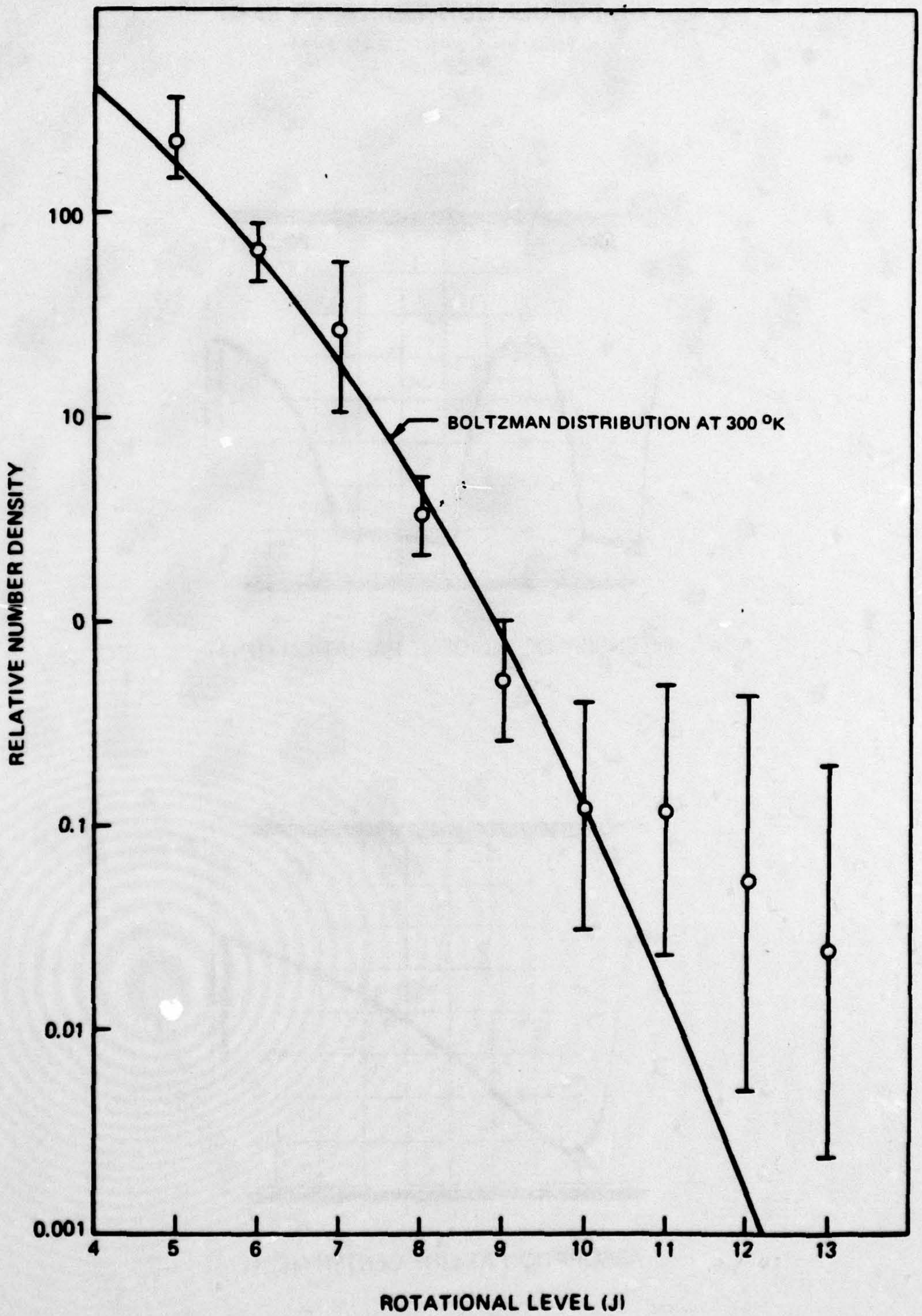
Pump Line	$\frac{\text{excess population}}{\text{Boltzmann population}}$ (%)
1P10	13.6
1P11	11.5
1P12	16.5
1P13	13.3
1P14	10.0
	13 ± 3%

REFERENCES

1. Shin, H. K.: Chem. Phys. Lett. 10, 81, 1971.

2. Wilkins, R. L.: The Aerospace Corporation Reports SAMSO TR-77-197, SAMSO TR-78-85 and SAMSO TR-78-89.

POPULATION DISTRIBUTION IN V = 0 AFTER V TO R TRANSFER



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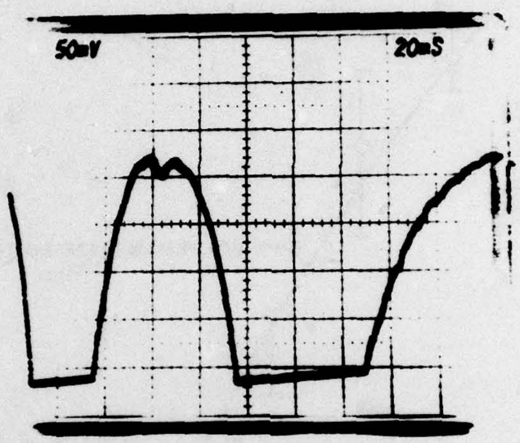
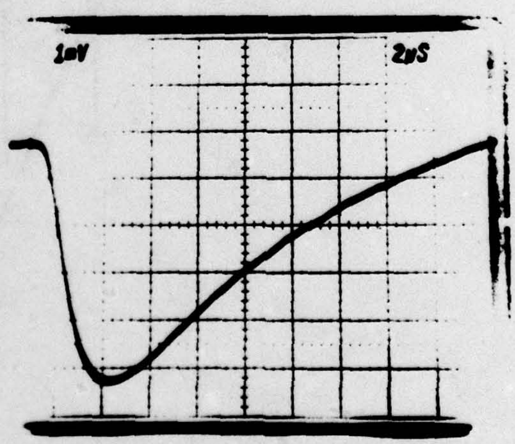
V-R POPULATION TRANSFER IN DF

FROM V = 1, J = 3 TO V = 0, J = 11
0.07 torr



INTENSITY OF INCIDENT RADIATION (1P11)



ABSORPTION AT LINE CENTER (1P11)

LIST OF PUBLICATIONS

J. J. Hinchen and R. H. Hobbs. Rotational Population Transfer in HF. J. Appl. Phys. 50, 628 (1979).

J. J. Hinchen and R. H. Hobbs. Pressure broadened linewidths in the 2.5 μ band of HF and the influence of polymer formation. J. Opt. Soc. Am. 69, 1546 (1979).

Planned Publications

Rotational Relaxation Studies of DF using IR double Resonance.

Pressure Broadened Linewidths in the 3.5 μ band of DF.

Vibrational to Rotation Transfer in HF and DF.

One the Relationship Between Rotational Relaxation and Linewidths in HF and DF.

Velocity Transfer Studies with HF Using IR Double Resonance.